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SCIENTIFIC PROCEEDINGS

OF THE

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Ohio Mechanics' Institute, 55th Annual Report, 1883.
Cincinnati Museum Association, 1st Annual Report, 1882.
Cincinnati Water Works, 43d Annual Report, for 1882.

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SCIENTIFIC PROCEEDINGS
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OHIO MECHANICS' INSTITUTE.

VOL. II. SEPTEMBER, 1883. No. 3.

X.—MECHANICAL NOTES.

BY HARRY M. LANE.

[Read before the Section of Mechanics and Engineering, April 24, 1883.]

I. FRICTION OF SLIDE VALVES.

IN discussions relating to the best form, proportions, and number of ports for steam engines, two points have frequently been considered, namely: the frictional resistance to steam in entering and leaving the cylinder, and the area of the cooling surface with which the live steam comes into contact after the surface has been exposed to the reduced temperature of the exhaust. It seems important that we should also consider the power required to move the valve covering the port or ports of the particular form, dimensions, and number, which a consideration of the first two points may lead the designer to adopt.

To show at a glance the relative value of various port arrangements, when measured by the power required to operate their valves, the novel method represented by the accompanying diagram has been adopted.

Five different arrangements have been selected, which indicate all principal variations in proportion and number.

The port area is four square inches in each case, and other dimensions are as follows:

Fig. 1.—One port, square, 2 x 2 inches.
Fig. 2.—One port, oblong, 1 x 4 "
Fig. 3.—One port, " ½ x 8 "
Fig. 4.—Two ports, each ½ x 4 "
Fig. 5.—Three ports, " ½ x 2⅔ "

Actual steam pressures are ignored, as being unnecessary, since comparison only is desired. The mean unbalanced area of the valves, multiplied by the travel, is taken as the basis for calculation.

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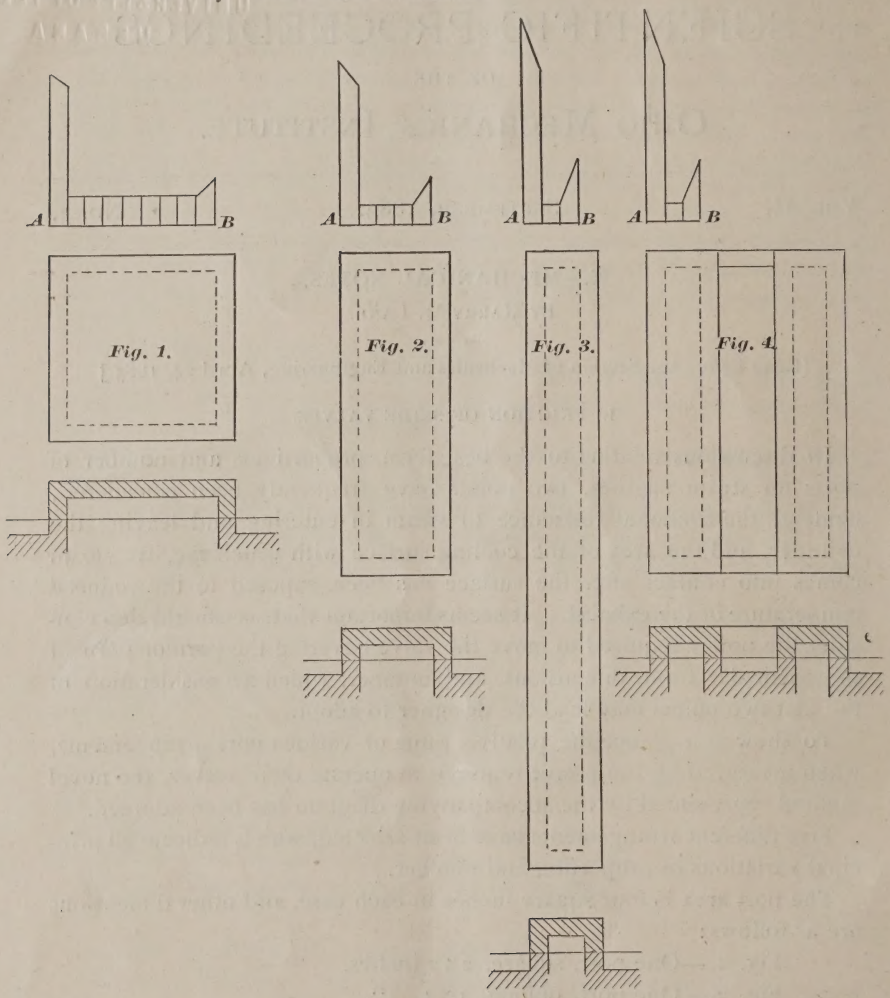
The travel of the valve is represented by horizontal, and the unbalanced area by vertical measurements.



AB is the travel line in each case, divided into ¼ inch spaces. On vertical ordinates is laid off the unbalanced area of the valve at the corresponding point of its travel. Each square inch of such unbalanced area is represented by a linear inch. The area of the completed figure represents the comparative power or work required to move the valve through its stroke, and the length of any vertical ordinate represents the

comparative force required to move the valve at the corresponding point of its stroke. These values, multiplied by the steam pressure (with proper reduction for the opposing effect produced by back pressure) and by the coefficient of friction, give the absolute values of work and force required.

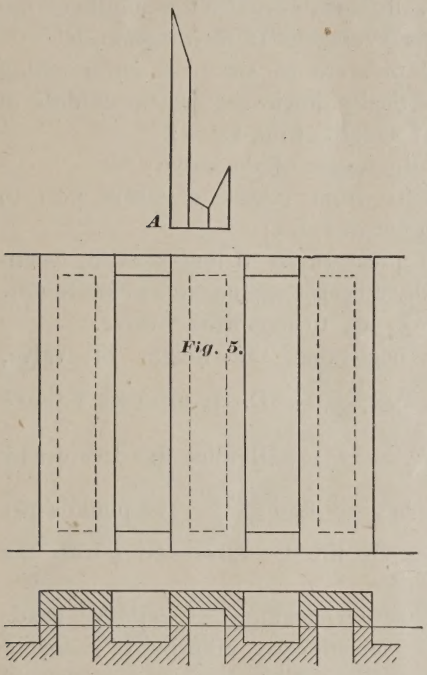


Fig. 5.

In engines of recent design, the general tendency seems to be toward an increase in the number of steam ports. From this diagram, however, we learn that diminished frictional resistance follows a lengthening of port and reduction of travel in the single port arrangement, and the same improvement is noticed in reducing the number by increasing the length in the multiport or "gridiron" arrangements. In addition to the disadvantage of requiring increased power to drive the valve, it will be noticed that the cooling surface and resistance to entering steam are also greater in the gridiron type. It therefore seems reasonable to conclude, that the greater the departure from the long single port, which admits of short valve travel, the greater will be our departure from attainable excellence.

II. THE SLIDE-VALVE AS A WATER RELIEF VALVE.

It is customary, in plain slide-valve construction, to allow free play of the valve between the collars or within the yoke by which it is driven, for the purpose of allowing it to be lifted from the seat, and thus to serve as a water relief valve, should the quantity of water in the cylinder render this necessary.

To estimate the cylinder pressure necessary to accomplish this, a sketch has been prepared (Fig. 6), showing a slide-valve in the position it would occupy when in the act of relieving the cylinder of water. The dimensions are from an actual engine of recent construction.

To lift the valve requires that the total pressure of the confined water

in the cylinder, acting vertically upwards, at the middle of the width of the steam port, multiplied by its leverage, shall be in excess of the pressure in the steam-chest acting vertically downwards at the middle of the length of the valve, multiplied by its leverage. In the diagram, let

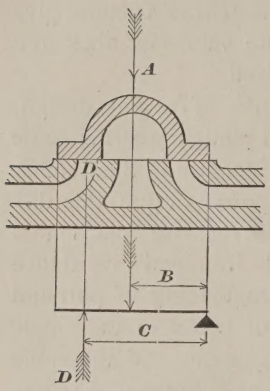


Fig. 6.

A = total pressure of steam in chest acting vertically downwards at the middle of the length of the valve;

B = half the length of the valve;

C = distance from middle of steam port to corner of valve;

D = total pressure in cylinder acting vertically upwards against area of steam port necessary to support the valve.

Then, neglecting the weight of valve, C: B:: A: D or $\frac{B \times A}{C} = D$. In this case we have $\frac{3\frac{3}{32}'' \times 5220}{5\frac{1}{8}''} = 3151$. Dividing this pressure by the area of the port in square inches we find $\frac{3151}{6.7} = 508$ pounds per square inch in the cylinder necessary to lift the valve and release the water.

Now it is customary to proportion the fastenings of cylinder heads etc. to resist the highest probable boiler pressure, allowing of course a proper factor for safety. It is evident that the required strength should be based upon the pressure required to lift the slide valve; as the area of the port is relatively small, this may be five times the boiler pressure.

III. COMPRESSION AND CUSHION.

The two terms "compression" and "cushion" are often used indiscriminately in steam engineering. According to Webster, compression is the act of forcing the parts of a body into close union or density by the application of force, and cushioning is the act of providing a soft resting-place. We can not do better than accept these definitions as indicating the distinction which it is desired to point out.

The nature and extent of compression are shown by a diagram from one end of the cylinder; its independent effect is purely economic, in that it increases the pressure and temperature in the clearance space, preparatory to the introduction of live steam, of which it is supposed to save an amount represented by the volume and pressure of the compressed

exhaust. The object of cushion is to bring the reciprocating parts gradually and gently to a state of rest at either extremity of the stroke, or to prevent "pounding on the centers"; we may have, in the same engine, and at the same time, an abundance of compression but absolutely no cushion.

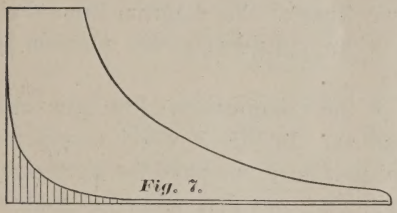


Fig. 7.

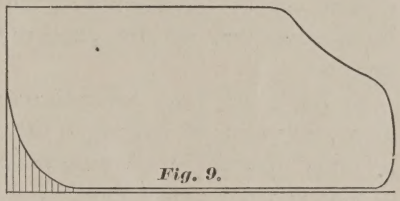


Fig. 9.

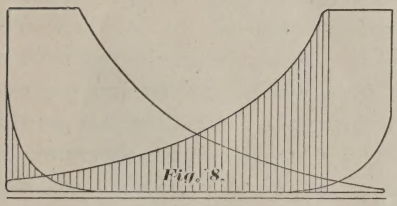


Fig. 8.

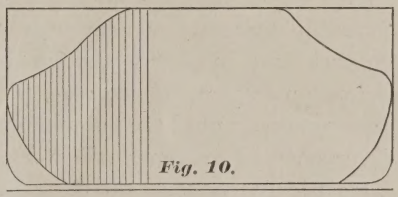


Fig. 10.

It has been stated that the nature and extent of compression may be ascertained by means of a single diagram from one end of a cylinder. In order to derive correct information concerning cushion, simultaneous diagrams from both ends of the cylinder must be referred to. By means of these, we ascertain the pressure on both sides of the piston at every point of its stroke; and it is the difference in pressure on the two sides that we must consider when studying the question of cushion.

The difference in pressure is readily ascertained from diagrams (reversed on the same paper as they are usually taken) by measuring from the steam line of one diagram to the exhaust line of the other.

If we begin anywhere near the middle of a pair of diagrams, or say previous to the fall of pressure due to the cut-off, and measure frequent vertical ordinates toward either end, we notice that the effective pressure is nearly uniform to the point of cut-off. It then becomes gradually less until we reach the exhaust closure of the other diagram, from which point the lines rapidly approach one another, until finally they meet and cross. Now at this point of intersection, the steam pressures on both sides of the piston are equal, and from this point our cushion begins; for the preponderance here changes from one side of the piston to the other.

The pressure (which now becomes cushion, or pressure acting in opposition to the direction of motion of the reciprocating parts) gradually increases, and offers an increasing resistance to the progress of the piston; until, if properly arranged, it will bring it gently to rest at the end of the stroke.

It is with the divergence of the two lines of the diagram from their intersection that we are concerned when considering the question of cushion.

In Fig. 7 we have an indication of the compression; but from this alone, no means of judging of the cushion. In Fig. 8, which represents a double diagram in all respects equal to Fig. 7, we have the deficiency of the single diagram supplied, and from it we may determine the cushion. Fig. 9 affords all necessary information concerning the compression of an engine with a later cut-off, and Fig. 10 (a double diagram from the same) shows the existence of compression without cushion; the intersection of the two lines, indicating the equalization of pressure on the two sides of the piston (which indicates the point from which compression begins), does not occur until the completion of the stroke; instead of that gradual divergence of the lines, as in Fig. 8, we have the lines separating in diametrically opposite directions, due to the rise of pressure occasioned by the incoming live steam on one side of the piston, and the fall of pressure occasioned by opening the exhaust valve and relieving the pressure from the opposite side; the combined effect is a blow on the piston represented by the sum of the increase and decrease of pressure.

It seems probable that confusion concerning the independent effect of the two operations under consideration may account for many cases of pounding; for a sufficient compression, as shown by a single diagram, is generally accepted as evidence that no alteration of exhaust valve action would prove a remedy in case of a pounding engine.

XI.—TARTRATES OF ANTIMONY.

By Charles Seth Evans, B. S.

[The substance of this paper was presented before the Section of Chemistry and Physics, April 26, 1883, and was embodied in a graduating thesis for the University of Cincinnati.]

This paper will deal chiefly with the simple tartrates, including their history and my own experimental investigation.

I.—HISTORY.

Berzelius describes two salts, in his *Lehrbuch*, 5te Aufl., **3**, 1124. He calls the first "tartrylsaures Antimonoxyd," and gives it a formula equivalent to Sb_2O_3, $3C_4H_4O_5$, or $Sb_2(C_4H_4O_6)_3$. This salt, he says, is formed by dissolving antimonious oxide in tartaric acid, is easily soluble, crystallizes in four-sided prisms, and is deliquescent in the air. The remarkable statement is added that the formula is grounded only on the probable supposition that the salt must have this composition, but that it had not been analyzed. The second salt is described as follows: When alcohol is added to solutions of the first salt, a white granular precipitate is formed, which has the composition of "1 At. Antimonoxyd" and "1 At. Tartrylsäure"; that is, Sb_2O_3, $C_4H_4O_5$. This salt, he says, loses one molecule of water of crystallization at 100°, and one molecule of water of constitution at 190°, becoming Sb_2O_3, $C_4H_2O_4$. It is insoluble in water, but forms many double salts.

A paper by M. Eug. Péligot on "La composition des sels d'antimoine,"* read before the Académie des Sciences, Oct. 12, 1846, describes a crystalline and a precipitated tartrate of antimony. The former, he says, is formed after a long time in a sirupy solution of the tartrate of antimony obtained by dissolving the oxide in tartaric acid; the salt crystallizes in right rectangular prisms, is very soluble in water, and deliquescent in moist air. The formula assigned is equivalent to $Sb_2C_{16}H_{32}O_{31}$. To represent the radical of tartaric acid, as now understood, this may be written $Sb(C_4H_5O_6)_2OH{\cdot}2\frac{1}{2}H_2O$. Péligot's numbers are given in the following table; but as he used a multiple of the old Berzelian atomic weight for antimony, 129·04, the theoretical percentages are recalculated with Sb=120.

	Found.		Theory, Péligot.	Theory, Sb=120.
Carbon	18·9 [1]	19·0 [2]	19·6	20·0
Hydrogen	3·5	3·5	3·2	3·3
Antimonious oxide	31·5	...	31·2	30·0
Water, 3½ mol	...	...	...	13·1
Loss at 160°	23·1 [3].			

[1] ·815 grm. salt gave ·566 CO_2 and ·263 H_2O.
·952 " " ·348 Sb_2S_3.

[2] ·703 " " ·490 CO_2 and ·227 H_2O.

[3] 1·688 " lost ·343 H_2O at 160°.

* Reported in abstract in Compt. rend. **23**, 709 (1846); in full in Ann. chim. phys. [3] **20**, 289 (1847). A translation of the latter paper (with the same discrepancy in the numbers) is found in Jour. prak. Chem. **41**, 376 (1847).

The last figure in this table does not accord with the data in the foot-note, which would indicate a loss of only 20·32 at 160°; this discrepancy is probably due to a misprint of 1·688 for 1·488. This item is of little practical moment, for at the temperature selected the acid radical would probably undergo dehydration to an uncertain amount. It is quite probable that the water of crystallization exceeded 2½ mol.; while the low percentage of carbon with high percentage of antimony would indicate the probable admixture of some more basic salt.

Péligot's second salt was precipitated by alcohol from a concentrated solution of the first. This was analyzed (but only after drying at 160°), with the following very imperfect results. No antimony determination was published.

	Found.	Theory, for $Sb\,C_4\,H_3\,O_6$.
Carbon	16·4	17·2
Hydrogen	1·3	1·0

The formula equivalent to $Sb\,C_4\,H_3\,O_6$ thus assigned by Péligot may be derived from $Sb\,C_4\,H_5\,O_7$ by dehydration; and the analysis indicates the probability that such dehydration at 160° was partial only.

Berzelius and Péligot have thus each independently described two salts of similar preparation and properties; the formulas assigned may be expressed as follows, where T represents the bivalent acid radical $C_4\,H_4\,O_4$:

	Berzelius.	Péligot.
Crystalline	$Sb_2\,(O_2T)_3$	$Sb\,(O\text{–}T\text{–}OH)_2\,OH$
Precipitated	$Sb_2\,(O_2T)\,O_2$	$Sb\,C_4\,H_3\,O_6$

In Watts' Dict. Chem. **5**, 683, three tartrates of antimony are described. The first is called "neutral antimonious tartrate," $(Sb\,O)_2\,C_4\,H_4\,O_6\cdot H_2\,O$. This is the precipitated salt of Berzelius, with its water of crystallization, and the account given in Watts is taken directly from him, but is credited to Péligot. The second, a "hyperacid salt," is the crystalline salt of Péligot. To it is given the formula $(Sb\,O)_2\,C_4\,H_4\,O_6\cdot 3\,C_4\,H_6\,O_6\cdot 5$ aq., which may be written—

$$Sb\left\{\begin{matrix}O\text{—}T\text{—}OH\\O\text{—}T\text{—}OH\\OH\end{matrix}\right.+2\tfrac{1}{2}\text{ aq.}$$

This formula is given without the least shadow of a doubt upon its composition; while, in fact, as we have seen, Péligot's figures are not consistent with any formula. The third salt described in Watts is an "acid antimonious tartrate," the precipitated salt of Péligot; it is said that it has the formula $C_4\,H_5\,(Sb\,O)O_6$, that it is formed by the addition of alcohol to a concentrated solution of the hyperacid salt, and

that it gives off one molecule of water at 160°, leaving the salt $C_4 H_3 (Sb O) O_5$. These statements, which are attributed to Péligot, are largely based upon opinions of chemical analogy. Moreover, Professor F. W. Clarke and Miss Helena Stallo prepared in the laboratory of the University of Cincinnati a compound having the formula $C_4 H_5 Sb O_7$*, whose unstable properties show that it is very different from Péligot's precipitate.

In view of these facts the subject needs a thorough revision. Statements utterly devoid of proof have been copied and re-copied, with nothing to indicate their doubtful character. My own investigation was to settle the composition of these salts, and to show how they could be formulated rationally, as derived from trivalent antimony, without the intervention of the univalent basic group Sb O.

II.—EXPERIMENTAL INVESTIGATION.

Throughout this work I have estimated the antimony by precipitating a hot, slightly acid, aqueous solution of the salts with a stream of hydrogen sulphide in excess; carbon dioxide was then passed through to make the precipitate more granular and more easy to wash. The antimony sulphide was collected on a weighed filter and dried at 90°–100°. The error arising from free sulphur in the precipitate was eliminated by heating a weighed portion of it in an atmosphere of carbon dioxide. This method of estimating the antimony has many advantages and disadvantages; the use of a weighed filter is involved, and seven weighings are necessary, viz.: two for the salt, two for the weighed filter, two for a porcelain boat before heating in carbon dioxide, and one after heating. These disadvantages, together with the slow drying of the precipitate, make the estimation long and introduce experimental errors. The carbon and hydrogen were estimated as usual by combustion with copper oxide.

1.—*The Precipitated Salts.*

Though both Berzelius and Péligot describe a single precipitated salt, I have found that there are at least three simple tartrates of antimony which may be obtained by precipitating as many solutions of antimony in tartaric acid, each containing a different quantity of the metal.

Salt No. 1.—This salt was obtained in the form of a white, curdy precipitate on adding alcohol to a solution of antimonious oxide in a considerable excess of tartaric acid. The precipitate was washed with alcohol and dried over sulphuric acid to a white amorphous mass. It was easily soluble in water and slightly so in alcohol. I found it impossible to dry

* Amer. Chem. Jour. **2**, 319, (1880).

the salt, even at 100°, as it melted to a thick gum. I have found it advisable in working with these salts to redissolve them in water and reprecipitate with alcohol; the salt comes down in coarser grains and dries more rapidly, with a less tendency to gum.

Analysis leads to the formula $Sb_2(O_2T)_3 \cdot 6H_2O$, where $T=C_4H_4O_4$, as follows:

	Found.	Theory.
Antimony	30·66 (mean) [1]	30·30
Carbon	18·14 [2]	18·18
Hydrogen (total)	3·01	3·03
Water lost at 155°–160°.	13·86 [3]	13·63

[1] ·3180 grm. salt gave ·1325 Sb_2S_3, or 29·76 % Sb.
·3725 " " ·1595 " " 30·58 "
·4441 " " ·1913 " " 30·76 "
·3633 " " ·1604 " " 31·54 "

[2] ·9233 " " ·6144 CO_2 and ·2503 H_2O.

[3] ·3486 " lost ·0483 H_2O at 155°–160°C.

Salt No. 2.—This salt was formed when alcohol was added to a solution of antimonious oxide in tartaric acid, obtained by boiling tartaric acid with an excess of the oxide. The white granular precipitate was filtered off, allowed to dry over night in the air, then redissolved in water and reprecipitated with alcohol. It dried over sulphuric acid to a white amorphous mass. The salt resembled in appearance the one just described; it dissolved easily in water, slightly in alcohol, and when it was collected it was supposed to be the same. Analysis agrees with the formula $Sb_2(O_2T)_2O \cdot 6H_2O$, as follows:

	Found.	Theory.
Antimony	36·55 (mean) [1]	36·36
Carbon	13·73 " [2]	14·54
Hydrogen	2·68 "	3·03
Water lost at 155°	16·32 [3]	16·36

[1] ·3441 grm. salt gave ·1777 Sb^2S^3, or 36·88 % Sb
·2350 " " ·1190 " " 36·23 "
·2677 " " ·1371 " " 36·55 "

[2] ·5621 " " ·2796 CO_2 or 13·56 % C, and ·1344 H_2O or 2·65 % H.
·7759 " " ·3955 " " 13·90 " " ·1896 " " 2·72 "

[3] ·2525 " lost ·0412 H_2O at 155°.

A portion of this salt was dissolved in water, and the solution allowed to evaporate spontaneously; it did not crystallize but dried into what the druggists know as a scale preparation—a clear, transparent, amber-

colored solid. This salt gave 16·39 per cent. of water (·7913 grm. of salt lost ·1297 H_2O at 165°), thus proving it to be the same hydrate as the original salt.

I was somewhat disappointed in this salt; for, when I found that it was not the same as the first one, I hoped that it might be the precipitated salt of Berzelius, to which he gives the formula $Sb_2 (O_2 T) O_2$, and which he says is insoluble in water.

Salt No. 3.—I determined to make one more attempt to obtain the salt of Berzelius; a quantity of tartar emetic was accordingly treated with dilute nitric acid, the precipitate was washed with water until the washings gave no reaction for nitric acid, and then boiled with fifty grammes of tartaric acid. The ratio of antimony to tartaric in the solution was about 4:5. There was an apparent excess of the antimonious oxide, for it would not dissolve entirely. The solution was precipitated with alcohol, the precipitate collected, washed with alcohol, and then redissolved in water and reprecipitated with alcohol. On being dried over sulphuric acid, it was more transparent than either of the other salts, and was all but insoluble in water. The analytical results approximate to the formula $Sb_2 (O_2 T)O_2 \cdot 2 H_2O$, as follows:

	Found.	Theory.
Antimony	53·73 (mean) [1]	52·63
Carbon	5·90 " [2]	10·52
Hydrogen	1·57 "	1·75
Water lost at 140°	7·79 [3]	7·89

[1] ·4539 grm. salt gave ·3407 $Sb_2 S_3$, or 53·62 % Sb
·3809 " " ·2872 " " 53·84 "

[2] ·5621 " lost ·1325 CO_2 or 6·43 % C, and ·0833 H_2O or 1·65 % H.
·5363 " " ·1059 " " 5·38 " " ·0732 " " 1·51 "

[3] ·7422 " " ·0578 H_2O at 140°.

The greatest difference between the theoretical and experimental percentages is in the carbon, which may have been due to an imperfect combustion, or to an admixture of $Sb_2 (OH)_3$ or basic salt.

This full series of tartrates precipitated by alcohol may now be compared in their graphical formulas with that for antimonious oxide; no evidence is found of the univalent radical, Sb=O, in place of hydrogen in tartaric acid.

Salt No. 1..... T=O_2=Sb—O—T—O—Sb=O_2=T + 6 H_2O
Salt No. 2..... T=O_2=Sb——O——Sb=O_2=T + 6 H_2O
Salt No. 3..... T=O_2=Sb——O——Sb=O + 2 H_2O
Oxide..... O =Sb——O——Sb=O

In closing the discussion of the precipitated salts, I can only express my regrets that lack of time compelled me to give up this work before I had proved beyond a doubt the existence of $Sb_2 (O_2T) O_2 + aq$.

2.—*The Crystalline Salts.*

Both Berzelius and Péligot state that when a sirupy solution of antimonious oxide in tartaric acid is allowed to stand for some time, a salt crystallizes out in right rectangular prisms. All the crystals which I have obtained from such solutions, whether the evaporation was spontaneous or over a water bath, have been rosettes of needles.

The crystalline product is not constant, but the antimony in it decreases as the tartaric acid is increased in the mother liquor; and if sufficient antimony be present, the solution will not crystallize at all, but dries up into a solid transparent gum. Those solutions which will crystallize are more viscous, the greater the amount of antimony that they contain. This viscosity of the mother liquor, together with the soluble character of the crystals, is an almost insurmountable obstacle in the analysis of these salts. It is all but impossible to free the crystals of a mother liquor which is so thick that the vessel may be inverted without spilling. With this condition of affairs, one can not be sure that he is dealing with a pure product, even after several recrystallizations. Another difficulty is met with in drying the crystals, especially those rich in antimony; for when placed over sulphuric acid they effloresce on the outside, while they remain soft and sticky inside.

Owing to the varying percentages of antimony in the crystals which were found in preliminary experiments, I was led to make a series of solutions containing different amounts of antimony, as follows:

A.—40 grams of $Sb_2 O_3$ were boiled with an aqueous solution of 60 grms. of tartaric acid for 24 hours. The solution was incomplete. The filtered solution was evaporated to dryness. The product will be described below. Sb=27·53 per cent.

B.—35 grams of $Sb_2 O_3$ were boiled with 60 grams of tartaric acid for 24 hours. This solution was still incomplete. It yielded crystals which could not be purified for analysis on account of the viscosity of the mother liquor.

C.—30 grams of $Sb_2 O_3$ were boiled with 60 grams of tartaric acid. The solution was complete. The crystals were washed and recrystallized twice.

D.—20 grams of $Sb_2 O_3$ were dissolved in 60 grams of tartaric acid.

The solution was complete and the product recrystallized. Several distinct lots of crystals were prepared at different times. The last product (**De**) was dried with extreme care and analyzed. The results are given below.

E.—15 grams of Sb_2O_3 were dissolved in 60 grams of tartaric acid. The product was twice recrystallized. The crystals, which were less sticky than when a larger amount of the oxide was used, yielded 5·37 per cent. Sb, and was probably a mixture containing free tartaric acid.

F.—12 grams of Sb_2O_3 were dissolved in 60 grams of tartaric acid. Product recrystallized. The product, though recrystallized, was a mixture.

The analytical data and results for the determinations of antimony are given in the following table:

A.	·4773	gram salt	gave	·1840	Sb_2S_3	or	27·53% Sb.
C.	·7587	"	"	·2010	"	"	18·92 "
Da.	·3751	"	"	·0701	"	"	13·35 "
Db.	·9668	"	"	·2153	"	"	15·90 "
Dc.	·8570	"	"	·1978	"	"	16·48 "
	1·0633	"	"	·2478	"	"	16·64 "
Dd.	·4979	"	"	·1114	"	"	16·18 "
	·7172	"	"	·1617	"	"	16·21 "
	·5554	"	"	·1334	"	"	17·16 "
De.	1·5341	"	"	·3847	"	"	17·88 "
	1·0843	"	"	·2733	"	"	18·00 "
E.	·5543	"	"	·0417	"	"	5·37 "
F.	·8839	"	"	·0443	"	"	3·69 "
	·4583	"	"	·0245	"	"	3·82 "

Salt No. 4.—The crystals **C** and **De** of the foregoing list had all the characteristics of definite compounds and proved to be $Sb(O\text{–}T\text{–}OH)_3 \cdot 4\,H_2O$, as the analysis will show.

	Found.			Theory.
	C	**De**		
Antimony.....	18·92 [1]	17·88 [1]	18·00 [1]	18·78
Carbon.....	22·59 [2]	22·98 [3]		22·53
Hydrogen.....	3·78	3·39		3·60
Water lost at 120°..	11·05 [4]	10·98 [5]		11·27

[1] See the table above.

[2] ·7201 gram salt gave ·5965 CO_2 and ·2449 H_2O.

[3] ·7945 " " " ·6727 " " ·2421 "

[4] ·9534 " " lost ·1054 H_2O at 120°.

[5] ·7218 " " " ·0793 " " "

This body, which may be called antimonio-tritartaric acid, is very soluble in water, effervesces strongly with carbonates, and behaves like a weak acid. If alcohol be added to its solution, the salt $Sb_2 (O_2 T)_3 \cdot 6 H_2O$, is precipitated.

Salt No. 5. —Solution **A** would not crystallize. A portion of its gummy solution was left upon the water-bath for 48 hours; upon cooling the tartrate was an amber-colored solid, which was ground up in an agate mortar to a straw-colored powder. This powder was analyzed, with the following results, and appeared to be $Sb\ (O\text{–}T\text{–}OH)_2\ OH$.

	Found.	Theory.
Antimony	27·53 [1]	27·58
Carbon	18·31 [2]	22·06
Hydrogen	2·96	2·53
Water lost at 105°	10·92 [3]	

[1] ·4773 gram salt gave ·1840 $Sb_2 S_3$.
[2] ·7201 " " " ·4836 CO_2 and ·1923 H_2O.
[3] ·7802 " " lost ·0852 H_2O at 105°.

The water estimation behaved in a very peculiar manner; for, though the salt was at no time heated higher than 105°, it lost in weight gradually for more than a day and a half. The percentage loss at successive weighings was as follows:

5·79, 6·85, 7·67, 8·15, 8·67, 9·02, 9·27, 10·21, 10·70, 10·92.

I am inclined to think that this loss in weight was due to a decomposition of the salt, for when alcohol was added to its solution, the precipitate had the composition of the precipitated salt No. 2, $Sb_2 (O_2 T)_2 O \cdot 6 H_2 O$.

Summary.—On comparison of the crystalline or acid salts with the precipitated or neutral salts, we have two series of tartrates, one derived from the antimony hydrate or the antimonious acid, $Sb\ (OH)_3$; the other from antimonious oxide $Sb_2 O_3$. Thus, neglecting the water of crystallization, we may write:

1	2	3	Oxide.
$Sb\{=O_2=T$	$Sb\{=O_2=T$	$Sb\{=O_2=T$	$Sb\{=O$
$Sb\{=O_2=T$	$Sb\{=O$	$Sb\{=O$	$Sb\{=O$
$Sb\{=O_2=T$	$Sb\{=O_2=T$	$Sb\{=O$	$Sb\{=O$

4	5	6	Hydrate.
$Sb\{O—T—OH$	$Sb\{O—T—OH$	$Sb\{O—T—OH$	$Sb\{OH$
$Sb\{O—T—OH$	$Sb\{O—T—OH$	$Sb\{OH$	$Sb\{OH$
$Sb\{O—T—OH$	$Sb\{OH$	$Sb\{OH$	$Sb\{OH$

It has been suggested to me by Prof. F. W. Clarke to call the tartrates derived from antimonious oxide, Nos. 1, 2, and 3, antimony tri-, di- and

monotartrate, respectively, and those derived from the hydrate, Nos. 4, 5, and 6, antimonio- tri-, di- and monotartaric acid respectively.

Of these I have obtained conclusively, as is shown in my figures, No. 1, the antimony tritartrate and its corresponding acid, No. 4. No. 2 was evidently formed, but No. 5, the antimonio-ditartaric acid, was obtained in rather a hypothetical manner. Great difficulty was experienced in even approximating to No. 3, the antimony monotartrate, while No. 6 was not obtained at all.

3.—*Double Salts and Other Derivations.*

From Antimonio-Tritataric Acid.—When barium carbonate is treated with antimonio-tritartaric acid, there is a brisk effervescence and the barium goes into solution, but on standing crystals of the ordinary barium tartrate are deposited. In another experiment the antimonio-tritartaric acid was neutralized with barium carbonate, and alcohol added to the filtered solution; a copious, white, granular precipitate was formed. After this was dried at the temperature of the air over sulphuric acid, it was partially insoluble in water, and gave the following percentages on analysis, approximately agreeing with $Sb_2(O_2T)_3 \cdot 4\,Ba(O_2T) \cdot 3\,H_2O$.

	Found.	Theory.
Antimony.....	12·47 [1]	12·77
Barium	28·27 [2]	29·17
Water lost at 150°..	2·45 [3]	2·87

[1] ·4071 gram salt gave ·0711 Sb_2S_3.
[2] " " " " ·1958 $BaSO_4$.
[3] ·3305 " " lost ·0071 H_2O at 150°.

It is doubtful whether this is a definite compound.

From Antimonio-Ditartaric Acid.—This compound behaved in every respect like the tritartaric acid. It was strongly acid, effervesced with carbonates, and was not precipitated by alkalies in the cold. Its solutions, when neutralized with barium carbonate and precipitated by alcohol, yielded a white curdy precipitate, which was dried over sulphuric acid. It did not dissolve entirely in water. A partial analysis agrees with the formula $Sb_2(O_2T)_2O \cdot 3\,Ba\,O_2T \cdot 11\,H_2O$:

	Found.	Theory.
Antimony.....	15·33	14·94
Barium.....	26·06	25·58
Water lost at 150°.....	12·66	12·32

[1] ·3801 grm. salt gave ·0818 Sb_2S_3
[2] ·3801 " " ·1685 $BaSO_4$
[3] ·4027 " lost ·0510 H_2O at 150°.

This is probably a mixture; though it (as well as the corresponding salt of the antimonio-tritartaric acid) may be weak double compounds.

A portion of the antimonio-ditartaric acid was neutralized with sodium carbonate; the liquid, which remained clear, was then mixed with alcohol. It immediately had the appearance of an emulsion, but later separated into two layers, both of which were clear, the lower one being decidedly yellow, and both contained antimony. The lower layer was sirupy and contained most of the sodium; it was accordingly drawn off by means of a separatory funnel. It evaporated at the temperature of the air over sulphuric acid to an amber-colored solid, which yielded a light yellow powder. Although a definite compound was hardly to be expected, the results of an analysis agree fairly well with the formula $2\ Sb(OH)_3 \cdot 3\ Na_2O_2T \cdot 3\ H_2O$. This salt was soluble in water and turned blue litmus paper faintly red. Its aqueous solution was not decomposed on boiling, but was precipitated by alkaline carbonates.

	Found.		Theory.
Antimony	24·66[1]	25·00[2]	24·54
Sodium	13·48[3]		14·11
Carbon	15·77[4]	15·64[5]	14·72
Hydrogen	2·62		2·45
Water lost at 150°	11·66[6]		11·04

[1] 1·0131 grm. salt gave ·3497 Sb_2O_3
[2] ·5290 " " ·1852 "
[3] 1·0131 " " ·4217 Na_2SO_4
[4] ·7091 " " ·4102 CO_2 and ·1673 H_2O
[5] 1·0844 " " ·6221 CO_2
[6] ·9493 " lost ·1107 H_2O at 150°.

Another portion of the antimonio-ditartaric acid solution was exactly neutralized with sodium carbonate; the fluid remained clear, but upon boiling deposited a heavy slimy precipitate, which was filtered off and placed over sulphuric acid, when it dried with extreme slowness to a light yellow solid, which was very insoluble in water. The filtrate from this precipitate, which was neutral, was treated with an excess of sodium carbonate, and the fluid boiled; a second precipitate was white and granular. This was also dried over sulphuric acid and was insoluble in water. Neither of the precipitates contained any sodium.

Both precipitates were analyzed. The first gave results which approximate to the formula $Sb_4O_5(O_2T) \cdot 12\ H_2O$, analogous to the sulphate $Sb_4O_5(SO_4)$ the chloride $Sb_4O_5(Cl)_2$, etc.

	Found.		Theory.
Antimony.....	47·87[1]	47·28[2]	51·95
Carbon.....	3·96[3]	4·24[4]	5·20
Hydrogen.....	3·44	3·21	3·03
Water lost at 155°.....	22·30[5]		23·37

[1] ·4652 grm. salt gave ·3118 $Sb_2 S_3$
[2] ·4543 " " ·3007 "
[3] ·6619 " " ·0962 CO_2 and ·2051 H_2O
[4] ·9316 " " ·1449 CO_2 and ·2695
[5] ·9102 " lost ·2030 H_2O at 155°.

The second precipitate was evidently antimonious oxide mixed with a little hydrate. Its analysis gave the following percentages:

	Found.	Theory.
Antimony.....	84·25[1]	83·33
Water lost at 150°.....	4·80[2]	

[1] ·7643 grm salt gave ·7297 Sb_2O_4
[2] ·7643 " lost ·0372 H_2O at 150°.

These results indicate the probability of a basic antimony tartrate, formed by the precipitation of the higher tartrates, as a step in the reduction of those higher tartrates to the oxide.

Antimony disulphato-tartrate?—A cold solution of antimony ditartrate, $Sb_2 (O_2T)_2O \cdot 6 H_2O$, was cautiously mixed with cold dilute sulphuric acid until it was faintly turbid, and then alcohol was quickly added. The white precipitate which formed was collected and dried over sulphuric acid; it contained antimony, sulphuric and tartaric acids, and water. It was insoluble in water. A partial analysis gave results which agree best with the formula $Sb_2 (O_2T) (SO_4)_2 \cdot 7 H_2O$. The results were:

	Found.		Theory.
Antimony.....	33·56[1]		33·99
SO_4.....	25·48[2]	25·52[3]	27·19
Water lost at 110°.....	12·31[4]		17·84

[1] ·3192 grm. salt gave ·1500 $Sb_2 S_3$
[2] " " " ·1974 Ba SO_4
[3] ·3684 " " ·2282 "
[4] ·3192 " lost ·0393 H_2O at 110°.

The antimony and sulphuric acids found are both decidedly low. The product may easily have been mixed with $Sb_2 (O_2T)_2 SO_4 + aq.$ and $Sb_2 (O_2T) (SO_4) O + aq.$ The fuller study of such derivatives is still open for investigation.

Tartrates of Silver and Antimony.—One or two double salts containing silver, antimony, and tartaric acid, were prepared in the following manner: An excess of silver tartar-emetic was dissolved in a comparatively

large amount of water; amyl iodide was then added; the yellow silver iodide was immediately precipitated, while the excess of silver tartaremetic remained in solution. The silver iodide was then filtered off, and the solution evaporated by boiling, until small crystals appeared upon the surface of the liquid; upon cooling, a large number of clear, small pyramidal crystals, which were almost insoluble in water, adhered to the bottom and sides of the vessel. An analysis of these crystals agrees best with the formula $Ag_2\ Sb_4\ (O_2T)_3\ O_4 \cdot\ 3\ H_2O$. The results were:

	Found.		Theory.
Antimony	37·37[1]	38·54[2]	38·15
Silver	17·19[1]		17·17
Carbon	11·21[3]	11·26[4]	11·45
Hydrogen	1·15[3]	1·21[4]	1·42
Water lost at 150°	3·43[5]		4·29

[1] ·2202 grm. salt gave ·0503 Ag Cl.
" " " ·1152 $Sb_2\ S_3$.
[2] ·6761 " " ·3648 "
[3] ·5144 " " ·2116 CO_2 and ·0532 $H_2\ O$.
[4] ·4533 " " ·1908 " ·0494 "
[5] ·6761 " lost ·0232 gr. water at 150°.

The formula of this salt may be written a variety of ways; the following (omitting the water) is symmetrical, with a fair distribution of electro-positive and electro-negative elements throughout the chain, but there is no proof of its symmetry or of the two closed rings.

$$Ag—O—T—O—Sb=O_2=Sb—O—T—O—Sb=O_2=Sb—O—T—O-Ag.$$

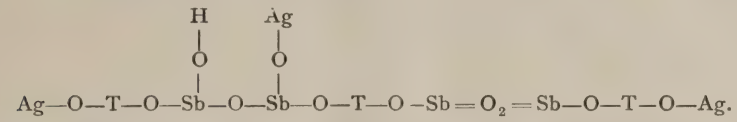
Several peculiar facts presented themselves in making the water estimation; the salt at 125° had lost 2·51 per cent. of water, and had turned the color of red lead; at 150° the loss was 3·43 per cent., and the salt had become very green and quite specular.

The preparation of the second salt was exactly similar to that of the one just described, except that ethyl iodide was substituted for the amyl iodide. The crystals resembled those of the first salt to a marked degree, but adhered more closely to the surface of the crystallizing dish. It was also insoluble in water. An analysis gave results which agree best with the formula $Ag_3\ Sb_4\ (O_2T)_3\ HO_5 \cdot\ 3\ H_2O$. The results were:

	Found.		Theory.
Antimony	33·37	[1]	34·70
Silver	21·61		23·42
Carbon	11·86	[2]	10·48
Hydrogen	1·16		1·37
Water lost at 150°	4·44[3]		3·90

[1] ·2838 grm. salt gave ·0815 Ag Cl and ·1326 Sb_2S_3.
[2] ·5287 " " ·2301 CO_2 and ·0552 H_2O.
[3] ·5611 " lost ·0258 water at 150°.

The graphical formula need not differ from the last, except in breaking one of the rings to attach Ag and OH,



This salt possessed the same physical properties as the first one, even to the change of colors in the water estimation. Neither of these salts, in treating with caustic potash, yielded any alcohol corresponding to the iodide which was used. The apparent difference of composition may be due to some admixture.

*Aniline Tartar Emetic.**—This salt was prepared by heating a solution of the barium tartar-emetic with aniline sulphate, and filtering to free the solution of barium sulphate. On standing over night, long, flattened, rectangular prisms separated out, the largest of which was about four centimeters. The first crop of crystals was dark purple, but on two recrystallizations they became nearly white; the gradations in color between the dark purple and pinkish white were very beautiful.

The salt is simply tartar-emetic, with aniline substituted for the potassium, and is devoid of water of crystallization. Its formula is $Sb\ (C_6\ H_7\ N{\cdot}H)\ O_3T$.

Antimony gave the following percentages:

	Found.	Theory.
Antimony.....	31·73 (mean)	31·74
·6101 grm. salt gave ·2574 $Sb_2\ S_3$, or 30·38 % Sb		
·8566 " " ·3911 " " 32·60 "		
·4028 " " ·1817 " " 32·22 "		

It should be stated, in conclusion, that in all the salts described above, antimony behaves as an ordinary trivalent metal. This may, therefore, be considered its normal condition in the simple tartrates and their analogues.

I can not close this paper without expressing my thanks to Professor F. W. Clarke for his constant aid and advice during a task of several months.

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* An account of this salt (with its specific gravity, 1·890) was published in Ber. d. chem. Gesel. **15**, 1540 (1882).

Note on Structural Formulæ of Tartrates of Antimony.

BY ROBT. B. WARDER.

While the preceding paper was in type, the "Researches on the Tartrates of Antimony," by Clarke and Evans, appeared in Amer. Chem. Jour. **5**, 241 (Sep. 1883).

The conclusions reached by Mr. Evans, as published above, admit of two interpretations. Peligot's suggestion of the univalent radical, —Sb=O, has been generally accepted without a question, but Professor Clarke and Miss Stallo proposed a different theory a few years ago;* both views may be thus illustrated in tartar emetic, when the formulæ are expanded:

$$K\text{–}O\text{–}CO\text{–}C_2H_2(OH)_2\text{–}CO\text{–}O\text{–}Sb{=}O \quad \text{(Peligot)}$$
$$C_2H_2(OH)_2\text{–}(CO\text{–}O)_2{=}Sb\text{–}O\text{–}K \quad \text{(Clarke)}.$$

According to Peligot, $C_4H_4O_4$ alone acts as an acid radical, while Sb=O simply replaces the hydrogen of carboxyl. According to Clarke's formula, on the other hand, Sb has a double character, replacing hydrogen, both in carboxyl of tartaric acid and in potassium hydrate, linking together a metal and an acid radical. It is hardly needful to point out the *a priori* improbability of such an arrangement, upon the electrochemical theory; for this formula seems to be withdrawn in the recent paper by Clarke and Evans, who now prefer to double Peligot's formula, thus:

$$K\text{–}O\text{–}T\text{–}O\text{–}Sb{=}O_2{=}Sb\text{–}O\text{–}T\text{–}O\text{–}K.\dagger$$

For Kessler's double salt of strontium tartar emetic and strontium nitrate,‡ they propose a formula equivalent to

$$NO_2\text{–}O\text{–}Sr\text{–}O\text{–}T\text{–}O\text{–}Sb{=}O_2{=}Sb\text{–}O\text{–}T\text{–}O\text{–}Sr\text{–}O\text{–}NO_2$$

but this is more simply explained by writing

$$NO_2\text{–}O\text{–}Sr\text{–}O\text{–}T\text{–}O\text{–}Sb{=}O,$$

which is combined with 6 H_2O, and, therefore, does not require to be doubled.

In conclusion, Peligot's hypothesis of a univalent radical, SbO, presupposes antimony "as an ordinary trivalent metal;" it is not antagonistic

* Ber. d. chem. Gesel. **13**, 1787 (1880) and Amer. Chem. Jour. **2**, 319, (1880).

† Loc. cit., p. 249. Compare also the formulæ suggested by Clarke in these PROCEEDINGS, **1**, 51.

‡ Pogg. Ann. **75**, 410 and Jour. prak. Chem. **45**, 361 (1848).

to the existence of "perfectly normal tartrates;" its occurrence is clearly proved in Sb_2O_3 and many other compounds; and no valid objection has been urged against its existence in tartar emetic or its derivatives.

XII.—DEVELOPMENTS IN THE KINETIC THEORY OF SOLIDS, LIQUIDS, AND GASES.

By H. T. Eddy, C. E., Ph. D., University of Cincinnati.

[Concluded from page 97.]

Part III.—On the Kinetic Theory of the Specific Heat of Solids.

In the second part of this paper, entitled *Kinetic Considerations as to the Nature of the Atomic Motions which probably originate Radiations* (pages 89–97), the author has given reasons in support of the hypothesis that the atoms of the different chemical elements are all composed of the same kind of ultimate atoms, which are in every respect equal and similar. Reasons were also given, tending to show that the vibrations of these ultimate atoms originate luminiferous and thermal radiations. And, further, an attempt was made to prove—in case radiations are due to vibrations of equal and similar ultimate atoms, which are set in vibration by the collisions of moving molecules—that two unlike masses of gas, which are in thermal equilibrium by radiation, will also be so when they are mixed; *i. e.*, when the equilibrium depends upon the collisions of molecules rather than upon radiation.

The object of the present paper is to consider the probable physical state of solid bodies, especially as to the amount of energy distributed among the different degrees of freedom possible in such bodies; and to show that the same hypothesis—of equal ultimate atoms—would cause solids, which are in equilibrium by radiation, to be also in thermal equilibrium when brought into contact; *i. e*, when the equilibrium depends upon the collisions of the molecules.

In the first place, let us notice what is apparently the mechanical significance of Dulong and Petit's law, which may be stated thus: The amount of heat which must be imparted to a chemical atom of a simple solid body to raise its temperature one degree is approximately the same for all the elements. Neumann has further shown that for compound solids, those of similar chemical composition require approximately the same amount of heat per chemical atom, but the amount is less than for

simple solids. There are, however, a few unexplained exceptions to these laws, which are due, possibly, to uncertainty as to atomic weights. The mechanical explanation of these experimental laws seems to be contained in the statement that in simple solids cohesion and chemism are one and undistinguishable; or, to express it otherwise, we may say that the molecules of simple solids are monatomic, the cohesion being of course much greater in some solids than in others. That this is a correct conception of the relations of the atoms of simple solids is made probable by various facts; among these it may be mentioned that mercury and cadmium, which are known to be monatomic as gases, as solids fulfill Dulong and Petit's law, and are therefore in the same physico-chemical condition as other simple solids.

Another fact is that already mentioned, to-wit, that the specific heat of atoms of compound solids is less than that of simple solids; and to this it may be added that the specific heat of simple solids is less when the volume is made smaller by hammering, compression, or cooling—which facts will be considered more at length later.

It is shown in the kinetic theory of gases, that when molecules of unlike gases are mixed together, the mean progressive energy of each molecule is the same, whatever its weight. Now, when a gas is in contact with a solid, will the collisions of the gaseous molecules with those of the solid cause the latter to have the same mean progressive energy of vibration as those of the gas? That will depend largely upon the duration of the collision. If the time occupied by a collision is so brief that only a small portion of a vibration of a solid molecule is described during the collision, then the laws of impulsive forces may be applied, according to which the effect of the finite forces, acting during the interval, may be neglected. In case the collision is brief, the distribution of the mean kinetic energy between the molecules of the gas and the solid will be very nearly the same as between different gases, and the mean kinetic energy of a simple solid molecule will differ little from that of a gas at the same temperature.

In cases, however, in which the modulus of elasticity of the solids considered is so great as to make the period of vibration of the molecules also brief, their mean kinetic energy would be materially smaller than in the previous case; and, if a solid could be found whose molecules were immovably fixed, no vibratory energy could be imparted to its molecules.

Now Dulong and Petit's law seems to show that all simple solids, even those having the highest modulus of elasticity, have an elasticity so small compared with that brought into action between molecules at the instant

of free collision, that the distribution of kinetic energy is approximately the same as if the body were gaseous and monatomic.

But since the laws of perfect elasticity require that the mean potential energy shall be equal to the kinetic, it follows that the specific heat of a simple solid should be approximately twice that of a monatomic gas at the same temperature and of the same atomic weight. The actual specific heats of mercury and cadmium gas would be of interest in this connection were they known, even though they could only be determined at temperatures far removed from those of their solids.

The foregoing statement has been based upon the assumption that any degree of freedom which suffers partial constraint, as do the degrees of freedom of translation of a gaseous molecule when it becomes solid, will have for that reason less kinetic energy imparted to it during molecular collision. This matter has been treated somewhat at length in previous papers upon the virial, but in this connection it may be useful to make a quotation from Thomson and Tait:* "If a set of material points are struck independently by impulses each given in amount, more kinetic energy is generated if the points are perfectly free to move, each independently of all the others, than if they are connected in any way."

This mechanical theorem has special application not only to the partial constraints introduced into the freedom of motion of molecules, when they change from a gaseous to a solid state, but it applies also to the additional constraints introduced into the degrees of freedom of solid atoms when those atoms become more closely bound together by chemism into groups or molecules. Evidently the bonds of union between the atoms of a compound solid molecule are such that these degrees of freedom are considerably more constrained than those which unite the atoms of different molecules; so that in compound solids the forces of cohesion and chemism are different and quite distinguishable the one from the other. Now what, according to the mechanical theorem above quoted, is the effect of introducing the additional constraints required in order to group a simple solid, or a mixture of simple solids, into molecules, and thus make it a compound solid? The effect will be to diminish the mean kinetic energy of the system as derived from the impacts of the molecules of any gas surrounding it. This is in fact what occurs, as appears from the experimental truth previously mentioned, that the specific heat per atom of compound solids is less than that of simple solids. How much the specific heat per atom is diminished should depend upon the intensity

* Nat. Phil., Art. 315.

of the chemical attraction, which certainly must be much greater than the cohesion between atoms of simple solids to cause such marked deviations of specific heat per atom as compound solids exhibit.

This result, when combined with that arrived at in connection with the discussion of Berthelot's law, in my paper upon *An Extension of the Theorem of the Virial, etc.*,* to the effect that the heat evolved in chemical decomposition is greater the greater the attractive force, enables us to enunciate the following law, the truth of which I am at present unable to verify for want of sufficient experimental data: Those solids, other things being equal, which evolve the greater amount of heat of chemical decomposition in changing from simple mixtures to compound solids, are those which have less specific heat per atom. The phrase, "other things being equal," in the above statement refers to the fact that compounds alone that are chemically similar are in strictness comparable. Many other circumstances, moreover, besides want of chemical similarity, may in special cases mask the experimental results, yet the truth of the law should be clearly recognizable in any general comparison of specific heats with the heat of formation of compound solids.

Similar principles evidently apply to the cases in which simple solids are permanently decreased in volume by hammering or compression, for then greater cohesive forces are brought into action, and the specific heat is diminished.

It remains to be shown, in conclusion, that thermal equilibrium, which has been established by collisions of gaseous and solid molecules, will continue to exist when its continuance depends upon radiations between equal and similar ultimate atoms, which are set in vibration by molecular collisions; or, to state it differently, it remains to be shown that the ultimate atoms of a gas and a solid in contact, each have the same mean vibratory energy with respect to each of their degrees of freedom, with respect to each other. This appears to be a direct consequence of the principles of constrained motion which have been considered in this and previous papers. It is only necessary that the impacts of a pair of solid molecules with each other should be such as to mutually impart and receive the same mean amounts of energy as those of a gas and a solid, to cause it to be a matter of indifference whether a given solid molecule is struck by another solid molecule or by a gaseous molecule, and when so struck each ultimate atom will receive its proper proportion of energy, whether it form part of a solid or of a gaseous molecule.

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* These PROCEEDINGS, **2**, 26–43 (March, 1883).

It is my intention to return to this subject hereafter, and to treat the vibrations of ultimate atoms more at length, in the hope of being able to show more precisely than has been done so far how the characteristic differences in the spectra of solids and gases exist.

IV. Liquefaction, Vaporization, and the Kinetic Theory of Solids and Liquids.*

In a solid, in which the molecules are evidently held at nearly fixed mean distances by cohesive and elastic forces, there are two kinds of partially constrained freedom of motion possible for each molecule as a whole; first a motion of its center in a small orbit of more or less irregular shape about a mean position; and second, a more or less irregular pendular motion of oscillation about a mean directional position. Both of these motions can be properly treated as vibratory motions, and the laws of force, under which the motions occur, though somewhat unlike, as will appear during the following discussion, have a general resemblance.

When a solid is liquefied, it is evident that the molecules slide on each other with facility, which is equivalent to supposing that the molecules of the body have become perfectly free as to directional position; and this may be explained by supposing that the pendular oscillation has been changed into rotation.

In order to give a clearer conception of how the mean potential and kinetic energies have been effected by such a change, let us consider the case of a simple pendulum, which may be taken to be a heavy particle suspended by a thin rigid rod. It is well known that for any small oscillation of this pendulum the mean potential and kinetic energies are equal, but for oscillations of more considerable amplitude this is far from being the case. In order to compare the mean potential and kinetic energies for larger amplitudes, it will be useful first, to make comparison in case of a body of unit mass falling freely through a height s under the action of gravity, in which case we must, in order to obtain the mean kinetic energy, compute the mean value of $\frac{1}{2}v^2 = gs$ during the fall. Let the mean value be denoted by a horizontal stroke

$$\therefore \tfrac{1}{2}\overline{v^2} = \overline{gs} = \frac{g\int s\,dt}{\int dt} \qquad (1)$$

* This part was published in Frank. Inst. Jour. [3] **86**, 8–17 (July, 1883).

Since by the laws of falling bodies

$$s = \tfrac{1}{2} g t^2 \qquad (2)$$

$$\therefore \tfrac{1}{2} \bar{v}^2 = \tfrac{1}{6} g^2 t^2. \qquad (3)$$

But the total energy, potential and kinetic, which is evidently constant during the fall, is by (2),

$$gs = \tfrac{1}{2} g^2 t^2, \qquad (4)$$

and this is, therefore, also the mean value of the total energy. We obtain the mean value of the potential energy by taking the difference of the means.

$$\therefore g(s - \bar{s}) = \tfrac{1}{3} g^2 t^2. \qquad (5)$$

Hence by (3) the mean potential energy in a free fall is twice the mean kinetic energy. The same result holds in case of a body sliding down a smooth inclined plane. This result may then be applied to oscillations such as occur in the ideal case of a perfectly elastic particle which rebounds from a horizontal plane, whether vertically or obliquely, as is the case when it slides down one incline of a **V** and then ascends the other without friction. We are now in a position to see what is the relation between the potential and kinetic energies in case a smooth particle oscillates by sliding down one branch of a **U** and ascending the other. In the lower part of the curve the velocity is near its maximum value, and as this part of its path is more extended than before, the mean kinetic energy is greater in the **U** than in the **V**. Were the parts of the **U**, which are nearly vertical, put at a more considerable distance asunder, the mean kinetic energy could be increased at will by so doing. Now, it is known, in case the curve on which the particle oscillates is a cycloid, that the mean potential and kinetic energies are equal. Hence, in case it oscillates by sliding on any smooth curve, such as a semicircle, whose vertical branches are not so far asunder as those of the cycloid which has a height equal to the radius of the circle, the mean kinetic is less than the mean potential energy. And it further appears that while for small oscillations the mean kinetic and potential energies are approximately equal, that as the amplitude of the oscillation increases, the mean kinetic energy is a smaller and smaller fraction of the total energy and of the mean potential energy. The same holds true in case the amplitude of the oscillation of the circular pendulum is pushed beyond 90° on each side of the mean. In fact, in case the kinetic energy at its lowest point is just sufficient to carry the particle to the highest point of the circle, the particle will rest there in unstable equilibrium, in which case

the mean kinetic energy will vanish, since the time of oscillation is then infinite and the total energy will become potential and remain so. Thus we see that the mean kinetic energy of the pendulum may be any fraction of the total energy less than one-half, according to the amplitude of the oscillation.

But there is one other circumstance of importance in this kind of oscillation, which is, that, although its total energy is constantly increased as the amplitude increases, it is far otherwise with the mean kinetic energy. This at first increases with the amplitude, though not so rapidly as the mean potential energy, but as the amplitude approaches 180° the time of oscillation is so greatly increased that the mean kinetic is actually decreased by an increase of amplitude. There is, therefore, a certain amplitude at which the mean kinetic energy is a maximum. What that amplitude may be, it does not now concern us to determine; the only point necessary to consider is the one stated, that an increase of total energy and a consequent increase of amplitude will in no case increase the mean kinetic energy unless the amplitude of the oscillation be carried to more than 180°. As has been seen, a considerable increase of total energy will serve only to diminish the mean kinetic energy, but if sufficient total energy be supplied to the pendulum the amplitude will exceed 180° and its motion will be changed from that of oscillation to revolution, and on sufficiently increasing the total energy the mean kinetic energy of revolution will be equal to the mean maximum kinetic energy of oscillation.

The application of the foregoing discussion to the oscillatory motion of the molecules of solid bodies is obvious. In case a molecule has one or more positions of directional equilibrium about which it oscillates, a sufficient increase of total energy (*i. e.*, heat) will bring its mean kinetic energy of oscillation to a maximum, and in order further to increase its mean rotary kinetic energy a large amount of potential energy (*i. e.*, latent heat) must be supplied to change the oscillations into rotations of the same mean kinetic energy (*i. e.*, to melt the body).

There is one other point to be noticed in this connection, which is, that according to this theory the specific heat of a solid will in general increase as its temperature rises towards the melting-point, which is in general accordance with experiment. It would be necessary, however, in order that this should universally be the case, to show that the mean energy of the particular molecular motion which is the physical cause of radiant heat, is proportional to the mean energy of the motion which we are now discussing. It is generally thought that such a relation exists,

and it is certainly highly probable that the ratio between them does not change rapidly with the temperature.

The results which we have here obtained are not due to the fact that the force causing the oscillation considered was a special function of the amplitude, or of the distance of the particle from its mean position. The only vital point is that the oscillation shall be such that there shall be a maximum value of the mean kinetic energy. This remark has special application to the phenomenon of vaporization also, which we shall now consider. In vaporization the molecules are evidently removed to such considerable mean distances from each other that their paths are mostly free from mutual interference, while, before vaporization, the molecules are in no part of their paths free from mutual action and reaction.

In considering the forces which act along a line joining two molecules between which cohesive forces act, the phenomena of cohesion and of resistance to compression make it evident that the force with which a molecule is drawn towards its mean position, when their mutual distance is slightly greater than the mean, is one which at first increases with the displacement of the molecule from its mean position, but the displacement can not be large without carrying the molecules beyond the range of their mutual cohesion. If, however, their mutual distance be decreased, the force tending to restore a molecule to its mean position increases with the displacement, and in such a manner that no force can bring them into actual contact.

The cohesive force actually existing between the molecules of a liquid is so masked by the phenomena necessarily accompanying liquidity that its true character has been largely overlooked. There is, however, no reason, as we think, to suppose that the forces acting to prevent decrease of volume in a fluid are different initially from those resisting dilatation, or at least that they differ more than the same forces do in a solid body.

In order that we may make clear the relations between potential, kinetic and total energy in case of vibration under the action of molecular forces of this character, we shall in the first place discuss the subject of the relation between the law of force and the distribution of potential and kinetic energy somewhat in detail. The law of force in case of the pendulum already discussed is

$$y = \sin x \qquad (6)$$

in which y is proportional to the force acting to restore the particle to its mean position, and x is proportional to the displacement of the particle from its mean position at the origin measured along its path.

In case of a force varying as the direct first power of the displacement, the corresponding equation is

$$y = x, \qquad (7)$$

which is the equation of a line tangent to (6) at the origin, and hence, as before seen, for vibrations of small amplitude the two laws are approximately identical.

Now let a third law be assumed to be represented by an equation of a form such as

$$y = \tan x. \qquad (8)$$

Since (7) is also tangent to (8) at the origin, for vibrations of small amplitude, the laws of force expressed by (7) and (8) will cause vibrations in which the distribution of kinetic and potential energy is approximately the same. If, however, sufficient energy is imparted to the vibrating particle so that the amplitude is not small, it is not difficult to see that the mean kinetic energy no longer remains equal to the mean potential energy, as it is when the law of force is expressed by (7), nor is the mean kinetic energy the less of the two, as when the law is expressed by (6), but instead it is now the greater of the two. This appears perhaps most clearly from the consideration that this case more nearly resembles, than do the preceding, that of an elastic particle rebounding between two fixed walls, in which case the mean potential energy vanishes and the mean kinetic energy is the total energy. Hence, it appears that when (8) is the law of force, the ratio of the mean kinetic energy to the total energy is greater than one-half, and increases with the amplitude of the vibration. This is true not only for the law of force expressed by (8), but for any law which is represented by a curve passing through the origin, tangent to (7) and falling on the same side of (7) as (8) falls.

From similar considerations it appears that whenever the curve expressing the law of force passes through the origin and is tangent at that point to (7) and falls on the same side of (7) as does (6), the mean kinetic energy of vibration will be less than half the total energy. Since in (8) the force of restitution becomes infinite at both $+\frac{1}{2}\pi$ and $-\frac{1}{2}\pi$, the oscillation is confined within those limits.

Let us now further suppose a law of force which will give a curve not having a point of inflection at the origin as does (6) or (8), but nevertheless tangent to (7) at that point.

Such a law is given by the equation

$$y = e^{-\tan x} \sin x, \qquad (9)$$

if we take only that part of it lying between $x = +\frac{1}{2}\pi$ and $x = -\frac{1}{2}\pi$.

On the negative side of the origin the curve somewhat resembles (8), while on the positive side, after reaching a maximum value of y at a point a little beyond $x = \frac{1}{6}\pi$, the curve rapidly approaches the axis of x, and the force vanishes at $x = \frac{1}{2}\pi$. This is in effect a combination of the two previous cases, and corresponds evidently to the case of the molecules of a solid or fluid held at mean distances from each other which are fixed at a given temperature.

During one part of the vibration the mean kinetic energy is more than half the total energy, as has been just now shown, while during the other half the mean kinetic energy is less than half that amount. It will depend upon the precise relation between the two parts of the curve what the effect is on the whole. But it is perfectly evident that for large amplitudes the whole effect will be of the same character as if both parts were of the kind expressed by (6), and the mean kinetic energy is then less than half the total. But it is to be noticed that for certain amplitudes, which are not too large, the contrary effect is quite possible and the mean kinetic energy will be less than half the total energy. This is the kinetic explanation of the fact first established by Rowland,* that the specific heat of water slightly decreases as the temperature rises, from 0° C to about 30° C. A similar phenomenon has been observed in case of mercury.

But the most important conclusion which flows from the fact that the mean kinetic energy decreases with the amplitude is, that in this kind of vibration, also, there is a maximum value of the mean kinetic energy which can not be increased by increasing the displacement, unless the molecules be carried beyond the range of their mutual attractions. This is what occurs in vaporization with the resulting change of volume, and a large increase of the potential energy without increase of the mean kinetic energy.

As was shown in connection with the discussion of the oscillation of the pendulum, the character of the oscillation is unchanged when the value of x in (6) lies between $+\pi$ and $-\pi$, but entirely changes its character and becomes revolution if those limits are exceeded.

When the law of force is expressed by (7), the character of the vibration is unchanged, however great the amplitude of the displacement; and, similarly, in case the law of force is that expressed by (8), the

*On the Mechanical Equivalent of Heat, with Subsidiary Researches on the Variation of the Mercurial from the Air Thermometer, and on the Variation of the Specific Heat of Water. *Proc. Am. Acad. Arts and Sciences*, 1880.

general character of the vibration can not be changed however large the total energy imparted to the vibrating particle, and in this case the amplitude of the vibration evidently can not, under any circumstances, be increased beyond $\frac{1}{2}\pi$, but x must always lie between $+\frac{1}{2}\pi$ and $-\frac{1}{2}\pi$, so that as the amplitude approaches these limits the motion resembles more and more that of an elastic particle rebounding between a pair of immovable parallel walls at a distance π from each other.

When, however, the law of force is that expressed by (9), the amplitude of the vibration can not exceed $-\frac{1}{2}\pi$ in one direction under any circumstances, but in the other direction the amplitude can not exceed $+\frac{1}{2}\pi$ without a change from vibration to free motion.

The phenomena to be represented show that the same general relation holds for any law of force of which the curve has the general characteristics of (9), such as, for example, that part at the right of the origin of the curve

$$y = ax^{-2} - bx^{-5} \qquad (10)$$

in which y is the force and x the distance between the molecules.

Such a curve as (10) must represent the facts of nature more accurately than the relation between them proposed by Maxwell, and expressed by the equation

$$y = -bx^{-5} \qquad (11)$$

which was taken by him to express the force acting during an encounter. But the law of force during an encounter can not be supposed to differ from that existing during any state of nearness of the molecules, so that (11) is to be regarded merely as an approximate expression for a law like that of (9) or (10), in which the part of the ordinate of the curve expressing the attraction of the molecules is neglected. It must be noticed that the origin in (10) and (11) is differently situated from that in (9), as will be seen upon sketching the curve. The line $x = -\frac{1}{2}\pi$ in (9) is that taken as the axis of y in (10) and (11),

Having now considered in general the nature of the change which occurs in the molecular motion during vaporization, a somewhat closer consideration will enable us to see the remarkable mechanical significance of the so-called critical temperature, as well as that of ebullition. In ordinary evaporation into the atmosphere, without ebullition, only those molecules escape from the surface, whose kinetic energy is such as to enable them to overcome cohesion, and only so many can escape as will enable the vapor to fulfill approximately the law of Gay Lussac. The process by which the vapor tension in this case acquires its maximum value, is one whose velocity is regulated by the laws of gaseous diffusion,

when the vapor tension is less than the atmospheric pressure. But when the temperature rises to such a degree that the mean kinetic energy of the molecules (which, according to our theory, may be the same in both liquid and vapor) is greater than that of the superincumbent atmosphere, the vapor no longer merely diffuses from the surface, but is able mechanically to push back the atmosphere, or other pressure, to which it is subjected, and ebullition takes place. Even in the case of ebullition, however, only part of the molecules are able to free themselves from the force of cohesion, namely, those molecules which happen to have a kinetic energy so far above the mean as to carry them out of the range of the force of cohesion, and enable them to push back the superincumbent pressure. If, however, the temperature be still further increased, a point must at last be reached, whatever be the volume and consequent pressure, such that the mean kinetic energy is greater than the maximum possible in the liquid state. The liquid must then become a gas without regard to volume or pressure. The temperature at which this occurs is the critical temperature for the liquid considered.

There are then three kinds of vaporization possible, evaporation, ebullition, and gasification.

There appears, however, to be only one kind of liquefaction (melting) which is most nearly analogous to gasification, and without further reasoning it will appear that for those substances whose melting point is lowered by pressure, there must be a critical temperature of melting above which the body will be liquid, whatever be the pressure, *i. e.* no pressure can lower the melting point beyond a certain amount dependent upon the constitution of the body.

The results of these views as to the mechanics of liquefaction and vaporization are in general accordance with the hypothesis of Clausius,* who supposes that the mean kinetic energy or "real specific heat" does not depend upon the state of aggregation of the body, and they are in exact accordance in this particular that the mean kinetic energy need not be changed by change of state from solid to liquid or from liquid to gas. But whether the translatory motion of the molecules is the direct physical cause of radiant heat is still an open question which we shall discuss more at length in another place, where we shall also take occasion to discuss the relation between the specific heats of a body in its different states of aggregation, solid, liquid, and gaseous.

There is, however, one point which may perhaps be well considered

*Phil. Mag. [4] **24**, 204 (1862).

in this connection, and that is the explanation of the very large specific heat of liquids, compared with the same substances in the solid or gaseous state. This appears to be very probably due to the effects of the centrifugal force developed in the freely rotating molecules. The law of most probable distribution of rotary velocities shows that although the larger number of molecules are rotating with a velocity whose square is near the mean, yet all other velocities also exist, and among them very great ones.

Those rotary velocities which are sufficiently great will dissociate the atoms of the rotating molecules from each other, and the energy of rotation being expended against atomic forces will become potential and will not again become an available part of the kinetic energy until the atoms so separated meet others with which they can reassociate into molecules. A certain small per cent. of the total mass of the liquid must continually be thus dissociated in order that atoms may meet sufficiently frequently so that reassociation may be possible, and a uniform condition exist, in which as much reassociation happens as dissociation. This quantity must increase with the temperature, and the energy thus employed is apparently the reason of the high specific heat of liquids. In electrolysis these dissociated molecules are mechanically separated from the others, and to keep up the per cent. of dissociation a new supply is required for which energy must be supplied, just as it must be to preserve the temperature of a fluid from whose surface vapor is constantly being removed. A somewhat analogous phenomenon occurs in vaporization, but as it can occur ordinarily only at the surface, the analogy has been overlooked. A liquid gives off vapor at temperatures below boiling. According to the theory broached in this paper, only those molecules pass beyond the range of the cohesive forces whose kinetic energy is sufficiently above the mean to enable them to overcome the cohesive force and have still remaining on the average an amount of kinetic energy equal to the mean.

But this can occur only at the surface, for inside the mass of the fluid such molecules are entangled and soon lose this superfluous energy in encounters with other molecules. We may, perhaps, put the comparison in a clearer light by supposing a liquid, in which no such dissociation occurs, such as mercury probably is, and let it be in connection with a large closed space which is filled with the vapor of the liquid at its maximum tension. Now raise the temperature of the fluid and wait until the vapor in the closed space has reached the tension corresponding to this temperature. The heat supplied is partly employed in increasing the kinetic

energy, and partly in vaporizing a portion of the liquid, and is much larger in amount than would be required if there was no vaporization. In a quite analogous manner, the heat energy necessary to raise the temperature of water would probably be much less were there no dissociation accompanying the increase of temperature.

It appears from experiment that the specific heat of mercury is nearly the same in its solid and liquid states as it should be in case its molecules are monatomic in both states. It would be of great interest to know whether the specific heat of mercury gas has also the same value. It is noticeable that the latent heat of liquefaction of mercury is extremely small, which would lead to the hypothesis that the atoms of mercury are very nearly round and smooth, and that the rotary energy of a molecule of mercury is but a very small fraction of its total kinetic energy.

Cadmium, which is monatomic as a gas, would also furnish an interesting test of the theory, for it is not likely that the molecule of a substance greatly changes its character by change of state. Dissociation of the atoms of a molecule is evidently due to the motion of atoms away from each other. It is yet a question as to whether such oscillations can be caused in the atoms of a molecule as to absorb an appreciable amount of energy, or of such intensity that they can be caused to rotate. If such rotations are ever caused within the molecule itself, they probably occur at temperatures far above vaporization.

The conclusions to be drawn from the specific heats of elementary substances, whose molecules consist of but two like atoms, are in general confirmatory of the theory proposed in this paper, for the amount of rotary energy for such substances should be a less fraction of the total energy than in bodies consisting of a larger number of atoms, and the per cent. of dissociation should also be less. Now, in fact, for such bodies the specific heat in the liquid state does not, in general, greatly exceed that in the solid.

NOTES.

Influence of Time in Fertilizer Analyses.

BY ROBT. B. WARDER.

[The following note illustrates a practical application of the studies in dynamical chemistry undertaken by the Section of Chemistry and Physics. See page 51.]

Mr. H. A. Huston has examined the "influence of time and temperature on the amount of phosphoric acid dissolved from commercial fertil-

izers by citrate of ammonium."* From a sample of raw bone fertilizer containing 20·28 per cent. P_2O_5, ammonium citrate solution of 1·09 sp. gr. at 40° C. dissolved

In 30 minutes,	4·01	%	P_2O_5
" 45 "	4·97	"	
" 60 "	5·92	"	

Each of these values is a mean of three gravimetric determinations.

The solution was evidently incomplete. The chemical operations involved are somewhat obscure. Since a very large excess of citrate was present (about 40 mol. citrate to one of phosphate), we may apply the hypothesis that the rate of solution at each moment is proportional to the phosphoric acid still present that is capable of being so dissolved, or

$$\frac{-du}{dt} = au,\dagger \text{ and}$$

$$\log \frac{u_o}{u} = At.$$

According to this hypothesis, the most probable value for the limit of solubility, under the conditions of the experiment, is 7·8 per cent. of the raw phosphate, or 38 per cent. of the total phosphoric acid. For the calculated values below, $A = 0{\cdot}0107$.

	Percentage of P_2O_5 dissolved.		
Time.	Observed.	Calculated.	Difference.
30 minutes	4·01 (mean)	3·91	·10
45 "	4·97 "	5·05	·08
60 "	5·92 "	5·86	·06

The differences in this table are far less than those which appear in the several determinations upon which the means are based; yet this apparent agreement is no real proof of the hypothesis proposed or of the limit deduced, for which further experiments would be required. Mr. Huston very aptly emphasizes the importance of a uniform scale of time and temperature for determinations of reverted phosphoric acid. Some chemists are inclined to discard the citrate method entirely, as unreliable. The term "reverted phosphoric acid" is very objectionable, since it implies a previous solubility; but some test for relative present solubility is demanded by dealer and consumer. Far more concordant results can be expected if the reagent used is allowed to act until the limit is nearly reached, than if the time and temperature adopted allow but fifty or seventy-five per cent. of the soluble matter to be taken up. It will be seen, for example, from Mr. Huston's figures, that an error of a single minute in the time of action at 40° would result in an error of more than 0·06 per cent. "reverted phosphoric acid." The "Washington method"‡

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*Indiana Agricultural Report for 1882, pp. 230–233.

†This equation is explained and discussed in the paper on "Urech's Investigation of the Speed of Inversion of Cane Sugar," these PROCEEDINGS, **1**, 167–178 (Dec. 1882).

‡Proceedings of Convention of Agricultural Chemists held at Washington, D. C., July 28, 1880.

requires an exposure of the fertilizer to a solution of ammonium citrate at the ordinary temperature for an indefinite time (during elutriation, grinding, etc.) after which the "flask is put into a cold water-bath, the temperature is rapidly raised to 40° C., and there maintained for one-half hour." Under such conditions, great variations in the analytical results are inevitable. A summer temperature of 30° C. (according to Mr. Huston's results) effects solution about two-thirds as rapidly as at 40°; while the interval required to bring the temperature to 40° will vary greatly according to the size of the water bath and many other conditions. As a hint toward more accurate experiments in this direction, the hypothesis and figures stated above would indicate the solution of 7·6 per cent. of P_2O_5 in 9¾ hours, while 7·02 per cent. (or nine-tenths of the whole amount) would be dissolved in 2½ hours.

The desired uniformity of method for official analyses in the several States has not yet been secured;* a careful study of the dynamical phase of the problem may contribute to the selection of suitable conditions.

Purification of Drinking Water.

BY DR. F. ROEDER.

[Read before the Department of Science and Arts, May 10, 1883. Reported in *Science* I, 490 (June 1, 1883).]

From three to six drops of officinal dialysed iron, added to one liter of muddy water from the Ohio River, will precipitate the suspended solid matter. About two drops of the reagent are required to clarify water colored with one drop of blood. Albuminoids are removed by dialysed iron; perhaps, also, the other organic contamination. The precipitate, including all the iron, may be separated by filtration or decantation, leaving the water perfectly bright and transparent, and free from unpleasant taste or smell. For purification on a large scale, ferric chloride and sodium carbonate may be used in proper proportion. The small quantity of sodium chloride formed will not impair the taste of the water.

* The New Jersey law specifies a temperature under 38° C. (100 F.) for the solution of reverted phosphoric acid, with no limitation in regard to time. In a very interesting investigation conducted by the N. C. Agricultural Experiment Station, "the cold flasks were put into the bath warmed to 40° C., and left there forty minutes," in order to secure a "temperature of 40° C. in the contents of the flask for about thirty minutes." See Report for 1882, page 51. Results so obtained may be comparable among themselves, but are likely to differ from those of other observers.

Schedule of the Friday popular Scientific Lectures to be given by the Department of Science and Arts, during the season of 1883–4, at the Lecture Hall of the Institute, corner Sixth and Vine Streets, Cincinnati:

November 9. Professor T. C. MENDENHALL, Ohio State University.
Subject: The Electric Light.

December 14. Professor C. LEO MEES, Ohio University, Athens.
Subject: Molecular Motion and Crystallization.

January 11. Professor F. W. PUTNAM, Peabody Museum, Cambridge.
Subject: Ancient Arts of North American Nations.

January 25. Dr. ALFRED SPRINGER, Cincinnati.
Subject: The Cell and its Functions.

February 8. Professor E. S. MORSE, Salem, Mass.
Subject: Japan—its People and Industrial Occupations.

March 7 Professor THOS. FRENCH, JR., Cincinnati University.
Subject: Sound.

March 21. Professor W. L. DUDLEY, Cincinnati.
Subject: Water.

April 4. Professor T. H. NORTON, Cincinnati University.
Subject: Recent Advances in Chemical Technology.

April 18. Professor J. B. PORTER, Cincinnati University.
Subject: Mining and Metallurgy.